

## IONIC MASS TRANSFER ON FIXED DISK AND CONICAL ELECTRODES UNDER STREAMING SOLUTIONS—III. A SECOND EXPERIMENTAL APPROACH AND KINETIC APPLICATION\*

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**Abstract**—The rate of ionic mass transfer on fixed disk electrodes under streaming solutions was studied avoiding as far as possible any wall effect on the mass-transfer rate. Nickel electrodes, previously activated, and platinum and graphite electrodes with solutions of potassium ferro- and ferricyanide in sodium hydroxide were used. The geometry of the cell and other variables of the system were conveniently changed. The experimental rate equation agrees with that found by solving the Navier–Stokes and Fick's differential equations, for results with activated nickel electrodes, the fluid velocity being properly defined.

Results obtained with platinum and graphite electrodes present a deviation from those equations, a fact which is interpreted in terms of an electrochemical reaction with intermediate kinetics. The kinetic parameters of the corresponding electrochemical reactions are evaluated.

**Résumé**—La vitesse de transfert de masse ionique sur des électrodes à disques fixes dans des solutions agitées a été étudiée en obviant, autant que possible, à tout effet de paroi. Des électrodes de nickel préalablement activées et des électrodes de platine et de graphite ont été utilisées avec des solutions de ferro et ferricyanure de potassium dans l'hydroxyde de sodium. La géométrie de la cellule, ainsi que d'autres variables caractérisant le système, ont été modifiées. Pour les électrodes de nickel activé, l'équation de vitesse expérimentale concorde avec celle obtenue en résolvant les équations différentielles de Navier–Stokes et de Fick si l'on définit convenablement la vitesse du fluide.

Les résultats obtenus avec des électrodes de platine et de graphite manifestent par contre des déviations, interprétées en termes d'une réaction électrochimique de cinétique intermédiaire. L'on évalue les paramètres cinétiques des réactions électrochimiques correspondantes.

**Zusammenfassung**—Man untersuchte den Stofftransport an stationären Scheibenelektroden in strömender Lösung. Der Einfluss von Randeffecten auf den Stofftransport wurde möglichst klein gehalten. In Lösungen von Kaliumferro- und Kaliumferricyanid in Natronlauge wurden Nickel-, Platin- und Graphitelektroden verwendet. Die Zellengeometrie und andere Systemvariable konnten den Verhältnissen entsprechend angepasst werden. Die Messungen an aktivierten Nickelektroden stimmen mit den Ergebnissen der Berechnung des Stofftransports durch Integration der Navier–Stokes'schen und der Fick'schen Differentialgleichung überein, wenn die Strömungsgeschwindigkeit entsprechend definiert wird.

Die Ergebnisse mit Platin- und Graphitelektroden zeigen ein von den theoretischen Werten abweichendes Verhalten. Diese Tatsache wird darauf zurückgeführt dass hier keine reine Diffusionskontrolle vorliegt. Man ermittelte die kinetischen Parameter der entsprechenden Elektrodenreaktionen.

### INTRODUCTION

THE THEORETICAL rate equation, deduced in Part I,<sup>1</sup> indicates that the maximum rate of mass transfer, under convective-diffusion control in laminar flow, increases with the square root of the fluid velocity. In Part II,<sup>2</sup> a tubular electrolysis cell with axially placed conical and disk working electrodes was studied and it was observed that after formation of the Poiseuille profile the maximum velocity should be considered in the rate equation.

It is interesting now to study the ionic mass-transfer rate in circumstances similar to those already described,<sup>2</sup> but in a different type of electrolysis cell, where the incidence of the streaming solution is such that it takes place as if the influence of the counter-electrode wall on the process occurring in the working electrode were absent.

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This is equivalent to assuming that the velocity profile has a uniform distribution. It is therefore possible to take the average fluid velocity as the effective velocity in the rate equation. This assumption is tested in the present work, where a suitable electrolysis cell comprising the above mentioned possibility is described.

Another purpose of this study is to test the fixed disk electrodes as possible tools for hydrodynamic voltammetry, and consequently to study an electrochemical process the kinetics of which is no longer under convective-diffusion control. In this case the rate of ionic mass transfer is of the same order as the rate of the electrode-transfer process. As further described, an electrode process with intermediate kinetics is solved with the aid of those electrodes.

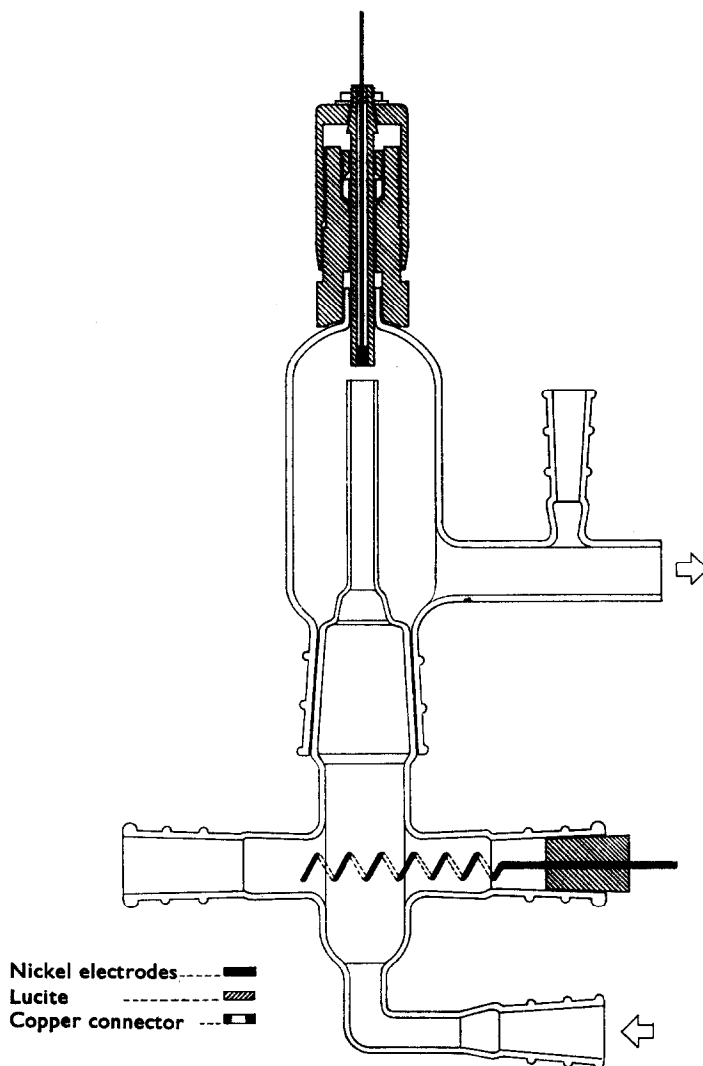


FIG. 1. Electrolysis cell.

## EXPERIMENTAL TECHNIQUE

## 1. Cell design

The electrolysis cell is shown in Fig. 1. Its body was made of Pyrex glass and the different parts were assembled by means of standard tapered glass joints. At the centre of the main body a vertical cylindrical tube was placed from which the streaming solution emerged; the open end of it was cut at right angles. Disk or conical electrodes were used. The disk electrodes consisted of a nickel, platinum or graphite rod, embedded into a Lucite rod with transparent epoxy resin. The working electrodes were

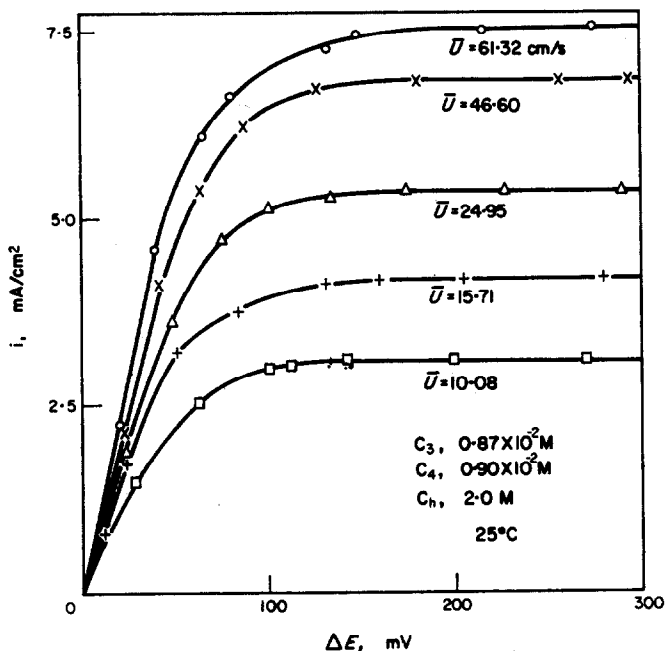


FIG. 2. Cathodic current/voltage curves. Nickel electrodes. Average flow rate is indicated in the figure.

vertically mounted, over the open end of the central tube, and they could be moved upwards or downwards by means of a micrometer screw fixed on the upper part of the cell, so that the distance between the outlet plane of the tube and the working electrode could be adjusted accurately.

The counter electrode was mounted in the lower part of the cell where a platinum wire employed as a reference electrode was also placed as usual. The electrolysis cell was assembled with the rest of the hydrodynamical circuit which comprised a glass-rotatory pump driven by a regulated ac motor, a flowmeter and a storage container, kept at a constant temperature in a thermostat.

## 2. Working conditions

Equimolar solutions of different concentrations of potassium ferro- and ferricyanide in 2 M sodium hydroxide as supporting electrolyte were employed. The concentration of the reacting species was changed from 0.003 to 0.1 M and was estimated by chemical analysis.

Tubes of three diameters were used, 0.39, 0.74 and 1.75 cm. The distance between the working electrode and the outlet plane of the inner tube was changed from 0.02 and 0.3 cm. The different working electrodes consisted of (i) nickel wires of 0.29 and 0.1 cm diameter (ii) platinum wires of 0.155 and 0.133 cm diameter (iii) a spectroscopic quality graphite rod of 0.30 cm diameter. Nickel electrodes were activated prior to use by connecting them as cathodes in a 5 per cent sodium hydroxide solution.

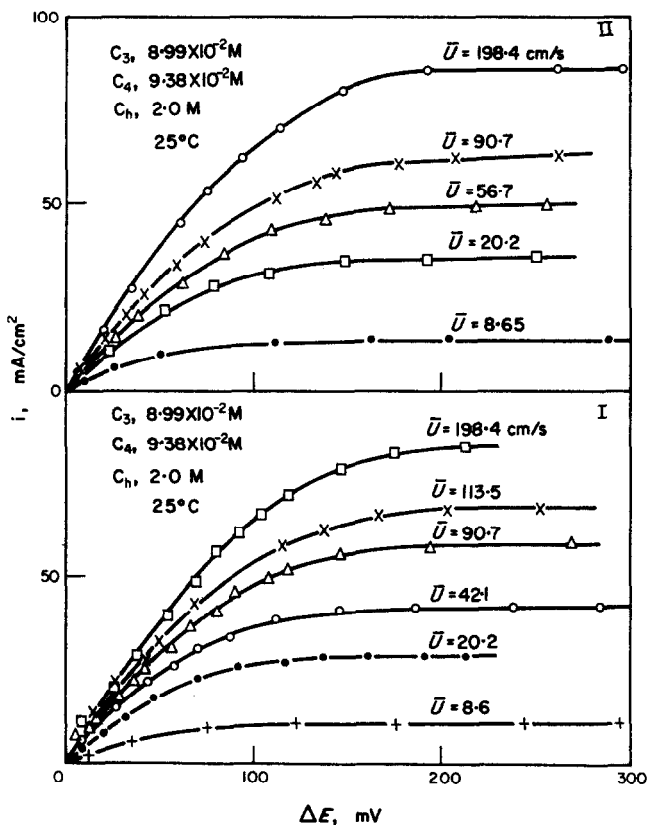


FIG. 3. Anodic (I) and cathodic (II) current/voltage curves. Platinum electrodes. Average flow rate is indicated in the figure.

Special care was taken in the design to avoid over-flooding of the cell. The flowing rate of the electrolytic solution was referred to the cross-section of the inner tube and it was varied from 1 to 400 cm/s.

Various series of experiments were also made with conical electrodes placed over the end of the central tube. Electrodes numbered from 9 to 13, indicated in Part II (Table 1),<sup>2</sup> were employed. These experiments were used to verify the generalization of the ionic mass-transfer correlation.

Current/voltage curves were determined as usual.<sup>2</sup> Both anodic and cathodic reactions were studied at 25°C.

## RESULTS

The experimental results were obtained for Reynolds numbers lower than the critical value. Results fall into three groups depending on the material of which the

working electrode was made. Typical results are presented in Figs. 2–4, for nickel, platinum and graphite electrodes, for both the cathodic and the anodic reactions.

### 1. Activated nickel electrodes

Current/voltage curves obtained with these electrodes show no appreciable activation polarization in the electrochemical reaction, as already established.<sup>3</sup> In this case

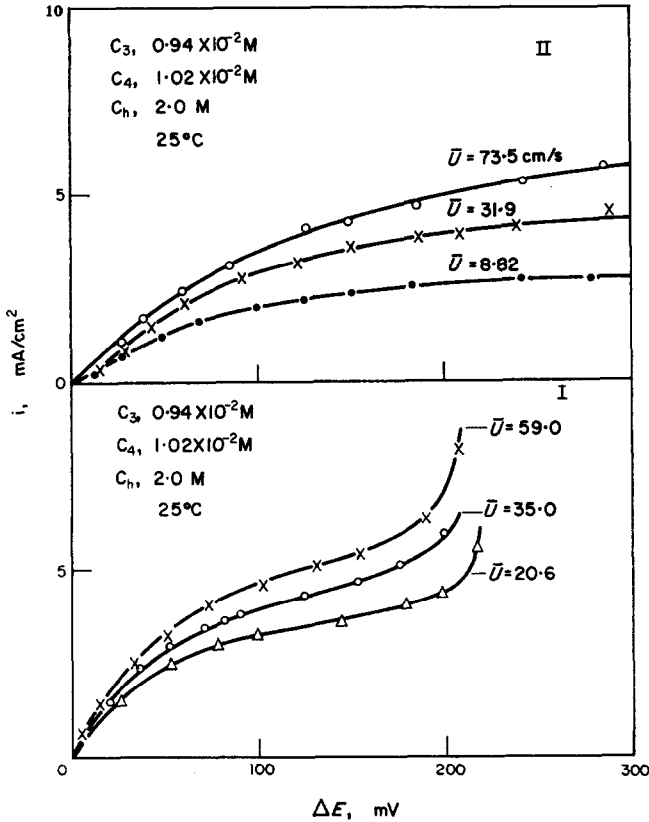


FIG. 4. Anodic (I) and cathodic (II) current/voltage curves. Graphite electrodes.

it was found that the limiting current density read at a constant potential increases linearly with the square root of the flow rate. As shown in Fig. 5, it appears that the relationship holds up to a flow rate of about 100 cm/s. The limiting current density is linearly dependent on the concentration of the reacting ion in the bulk of the solution. No dependence of the limiting current density on the distance between the planes of the working electrodes and the inner outlet tube was detected. The limiting current density at constant flow rate depends inversely on the square root of the radius. No appreciable effect of the length and diameter of the inner tube was observed.

Experimental data obtained for nickel disk and conical electrodes are plotted in Fig. 6 according to the equation deduced in Part I,

$$\text{Sh}_X = 0.78 \text{Re}_X^{1/2} \text{Sc}^{1/3}. \quad (1)$$

In this case the average fluid velocity was considered to define Reynolds' number.

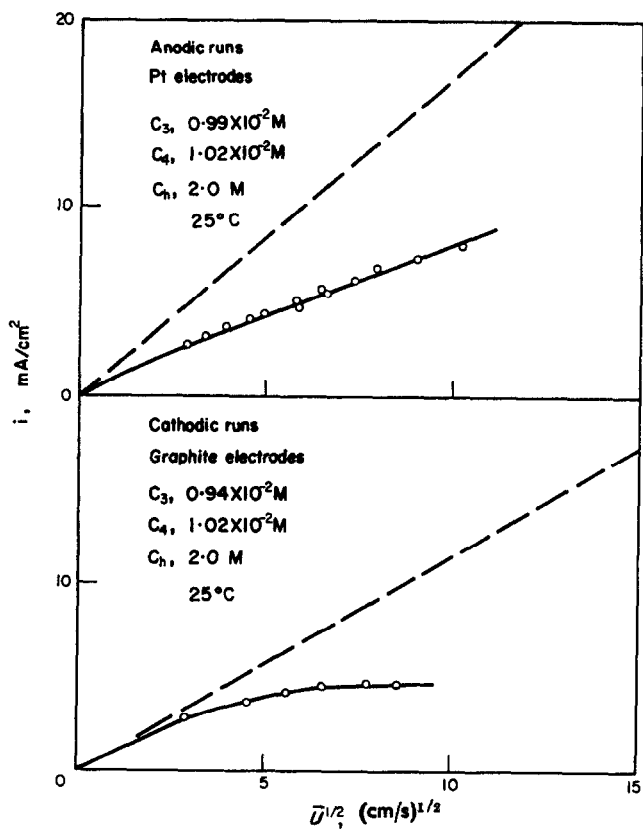


FIG. 5. Plot of the limiting current density vs the square root of the average flowing rate. Dotted line corresponds to (4).

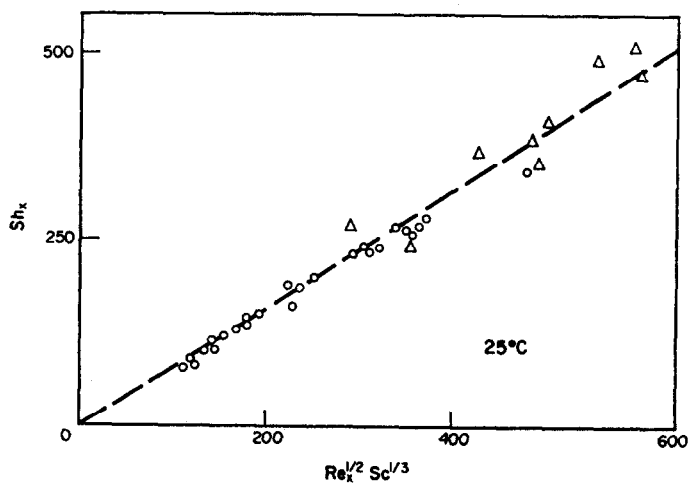


FIG. 6. Test of the dimensionless equation (1). Data obtained on nickel electrodes.

This is quite reasonable, since as a first approximation the velocity profile in the region where the fluid impinges on the electrode surface tends to become uniform. The lower the fluid rate, the better this assumption is fulfilled. For this reason data presented in Fig. 6 covered  $Re^{1/2}Sc^{1/3}$  up to 600. Beyond this point the data show some scatter as compared to the theoretical line. We thus conclude, that for a laminar flow the ionic mass-transfer correlation is valid also for this type of cell.

In spite of the scatter of the data, it is interesting to emphasize the coincidence of (1) at high flow rates, although a further comment is relevant. If some effect of turbulence increases the mass-transfer rate and if on the other hand the interference of any activated process involved in the electrochemical reaction is noticeable, these effects tend to compensate each other, and the correlation of results at high rates would be fortuitous. However, the reproducibility of results and the steady current observed during the experiments make an appreciable interference of these effects unlikely for the case of activated nickel electrodes. This can also be extended to the conical electrodes for values of  $Re^{1/2} Sc^{1/3}$  larger than 600 and up to 1300.

### 2. Platinum electrodes

As a first approximation the results obtained with these electrodes are comparable to those obtained with the nickel ones. In general this trend exists only for experiments performed at the lower flow rates. Data obtained at flow rates larger than 25 cm/s, as indicated in Fig. 5, show an increasing departure from the expected line, if the limiting current density at the same potential is plotted against the square root of the flow rate. It appears that under such conditions the limiting current densities for platinum electrodes are lower than those for nickel electrodes and the linear relationship is no longer obeyed.

### 3. Graphite electrodes

The apparent limiting current density for graphite electrodes also shows an appreciable deviation from what occurs under the same conditions for activated nickel electrodes at relatively low flow rates. The limiting current density appears as an asymptotical value at higher overpotentials. It is thus not possible to expect the type of linear relationship described before between the limiting current density and the square root of the flow velocity. The results obtained with platinum and graphite electrodes are not surprising if we consider the kinetic behaviour of the ferro-ferricyanide redox couple in aqueous solutions on these electrodes.<sup>4,5</sup>

## DISCUSSION

Results obtained with activated nickel electrodes confirm the validity of (1) in the new type of electrolysis cell, yielding further support to the theoretical approach of the ionic mass-transfer problem under laminar axial flow, at either conical or disk electrodes.

For the case of disk electrodes, the diffusion boundary layer width,  $\delta_d$ , can be presented in terms of the hydrodynamical boundary layer width,  $\delta_h$ , considering the dimensionless variable,  $\xi$ , already described.<sup>1</sup> We have

$$\delta_h = \xi_0 \sqrt{\left(\frac{v}{a}\right)}, \quad (2)$$

where  $\xi_0$  is the value of  $\xi$  when the dimensionless function approaches 1. As  $\delta_d$  and  $\delta_h$  are related by an expression such as

$$\delta_d = \text{const.} \cdot \delta_h \cdot \text{Sc}^{-1/3}, \quad (3)$$

we arrive at the conclusion that  $\delta_d$  is constant across the electrode area, so that from the diffusional viewpoint the surface is uniformly accessible as in the rotating disk electrode<sup>6</sup> and the translating electrode.<sup>7</sup> Consequently, the cell comprising a disk electrode with an axially flowing electrolytic solution becomes a promising device for kinetic study of electrochemical reactions.

Except for the activated nickel electrodes, experimental data obtained on other materials can be interpreted in terms of electrode processes with intermediate kinetics, following the reasoning already given for the translating electrode.<sup>7</sup> Equation (1) in terms of current density is

$$i_{\text{diff}} = 0.780 n_i F D_i \left( \frac{U}{\nu x} \right)^{1/2} \text{Sc}^{1/3} C_i^0, \quad (4)$$

where different symbols are as in Part I.<sup>1</sup>

Equation (4) can be extended to the region of intermediate kinetics, where, under steady state conditions, the rate of diffusional flow equals the reaction rate,  $\nu_r$ , on the electrode surface. The reaction rate can be written

$$\nu_r = k_r (C_i^s)^r, \quad (5)$$

where  $k_r$  is the specific rate constant referred to the unit area,  $C_i^s$  is the concentration of the reacting species on the electrode surface and  $r$  is the reaction order. In the steady state we have

$$D_i \left( \frac{\partial C_i}{\partial z} \right)_{z=0} = k_r (C_i^s)^r = \frac{i}{n_i F}. \quad (6)$$

The concentration  $C_i^s$  is obtained from the concentration profile (see (38) in Part I). Then we have

$$C_i^s = C_i^0 - \frac{i}{0.780 n_i F D_i \left( \frac{U}{\nu x} \right)^{1/2} \text{Sc}^{1/3}}. \quad (7)$$

The terms that depend on the properties of the solution as well as those depending on the geometry of the system can be represented by a constant  $A$ , which can be evaluated either from the theoretical considerations or from the analysis of the electrochemical reaction under mass-transfer control. From (6) and (7) we obtain

$$k_r \left[ C_i^0 - \frac{i}{AU^{1/2}} \right]^r = \frac{i}{n_i F}, \quad (8)$$

which involves two unknown parameters related to the electrode reaction itself. When  $r = 1$ , (8) becomes

$$i = \frac{n_i F k_r C_i^0}{1 + \frac{n_i F k_r}{AU^{1/2}}}. \quad (9)$$



When the rate of the activated process is much smaller than the rate of the diffusion process, (9) is transformed into one corresponding to an electrochemical reaction under activated control, where  $C_i^s \rightarrow C_i^0$ . Under these circumstances  $n_i F k_r \ll A U^{1/2}$ , since  $k_r$  is small, we have

$$i_{\text{kin}} = n_i F k_r C_i^0, \quad (10)$$

where  $i_{\text{kin}}$  is a limiting current density related to the activated process. (9) and (10) show that the current flowing through the system is lower than that expected from (4) if the electrochemical reaction involves intermediate kinetics.

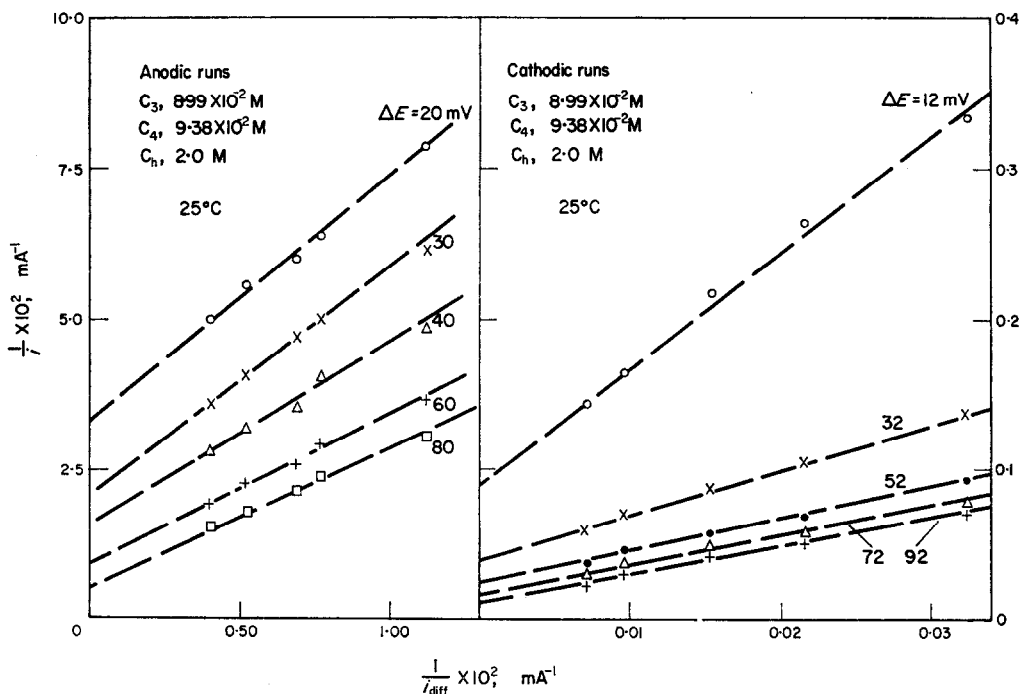


FIG. 7. Plot of  $1/i$  vs  $1/i_{\text{diff}}$  at different overpotentials. Platinum electrodes.

Let us now apply (9) to results obtained with platinum and graphite electrodes. Plotting afterwards  $1/i$  as a function of  $1/i_{\text{diff}}$  as shown in Figs. 7 and 8, straight lines are obtained one for each constant overpotential, having different slopes.  $i_{\text{diff}}$  is calculated with (4). Extrapolation of those lines to  $1/i_{\text{diff}} = 0$  yields the value of the current associated with the activated process at a fixed overpotential  $\Delta E$ . Then, from the well-known relationship between current and overpotential for activated processes,

TABLE 1

Reaction	Electrode	$C_i \times 10^3$ M	$b$ V	$\alpha$	$i_0 \times 10^3$ A/cm <sup>2</sup>	$k_r \times 10^8$ cm/s
Anodic	Pt	9.38	$0.086 \pm 0.005$	$0.69 \pm 0.05$	$22 \pm 2$	$2.4 \pm 0.2$
Cathodic	Pt	4.80	$0.107 \pm 0.010$	$0.55 \pm 0.06$	$12 \pm 2$	$2.6 \pm 0.2$
Anodic	graphite	1.02	$0.118 \pm 0.015$	$0.50 \pm 0.05$	$2.7 \pm 0.7$	$2.7 \pm 0.7$
Cathodic	graphite	0.94	$0.126 \pm 0.015$	$0.47 \pm 0.05$	$1.2 \pm 0.7$	$1.3 \pm 0.7$

the Tafel slope,  $b$ , the transfer coefficient,  $\alpha$ , and the rate constant at  $\Delta E = 0$ , for both the anodic and cathodic processes, can be evaluated. The more likely kinetic parameters related to the ferro-ferricyanide redox system, on platinum and graphite electrodes at 25°C, are assembled in Table 1. Those results agree satisfactorily with those earlier reported for the same reaction in similar aqueous systems for platinum<sup>5,9,10</sup> and graphite<sup>11</sup> electrodes.

We can therefore conclude that the present system is applicable to kinetic studies of electrochemical reactions. However, we must add that in the present case there

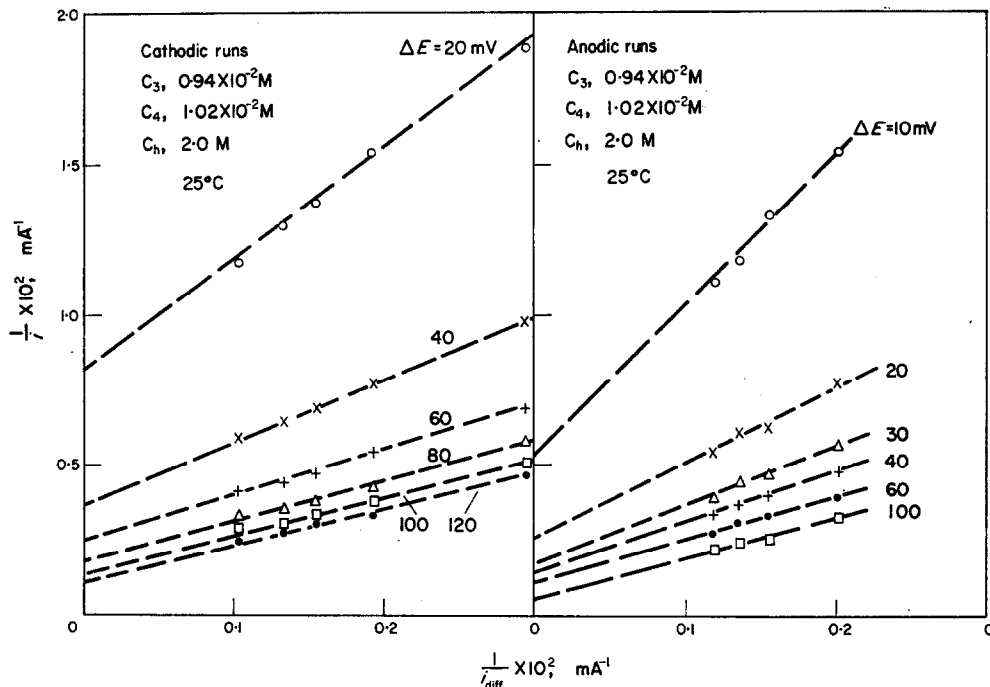


FIG. 8. Plot of  $1/i$  vs  $1/i_{diff}$  at different overpotentials. Graphite electrodes.

was an appreciable ohmic overpotential, which was considered in drawing the current/voltage curves. This difficulty was overcome by an accurate measurement of the ohmic drop between the working electrode and the capillary tip of the reference electrode with an adequate metallic tip and an ac bridge. In spite of the solution given here to this problem it would be advisable to improve further the electrochemical device just described in order to minimize the ohmic drop for future application.

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